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(54) Title: A PROCESS FOR PREPARING ALKYLATED DIHYDROXYBENZENE

(57) Abstract: The present invention relates to a process for the preparation of alkylated dihydroxybenzene by alkylating dihydroxybenzene with tertiary butyl alcohol in the presence of a solid/acid polymer catalyst.

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## A PROCESS FOR PREPARING ALKYLATED DIHYDROXYBENZENE

### Field of the invention

The present invention relates to a process for preparing alkylated dihydroxybenzene. More particularly, the present invention relates to a process for the preparation of alkylated dihydroxy benzene which is of use as antioxidant, polymer stabilisers, and in the treatment of mitochondrial respiration ailments, by the alkylation of dihydroxy benzene over solid acid or polyaniline sulfate as catalyst in the presence of a tertiary butyl alcohol.

### 10 Background of the invention

Friedel Crafts catalysis is one of the major industrially important processes that is widely used in the synthesis of low and high volume chemicals. Acylations, benzylations, alkylations and sulphonylations giving a wide range of useful products like ketones, alcohols, alkyl aromatics and sulphones are included in this reaction. 15 The petrochemical industry wherein a large number of alkyl hydrocarbons are produced by alkylation reactions is also a beneficiary of this reaction mechanism. The conventional catalysts used in this reaction mechanism include  $\text{AlCl}_3$ , HF,  $\text{H}_2\text{SO}_4$ ,  $\text{BF}_3$  and  $\text{BPO}_4$ . Most batch processes use  $\text{AlCl}_3$  as the soluble acid catalyst since it is a powerful Lewis acid and also inexpensive. However, it is difficult to handle  $\text{AlCl}_3$  and 20 other similar metal halides since they get easily hydrolysed. Very often these catalysts are required in stoichiometric amounts. A large inventory of these materials pose health, safety and storage problems. The traditional route of liquid phase alkylation using mineral acids and  $\text{AlCl}_3$  as catalyst suffer from the disadvantage of high capital costs, reactor corrosion, formation of by-products and the difficulty in catalyst 25 regeneration. In recent times, attention is being focused on development of environmentally friendly catalysts for the production of intrinsically important chemicals and chemical intermediates.

The use of safe solid acids in the place of traditional Friedel Crafts catalysts and mineral acids have become important. Several alkylation reactions of aromatic 30 hydrocarbons and functional aromatic hydrocarbons have been tried over zeolites, oxides, mixed oxides and supported oxides. Clays such as montmorillonite with an acidic function are also being considered as alternative catalysts for these reactions. Clays have also been modified for this purpose by pillaring with polyhydroxy metal

cations such as Zr, Al, Cr, Ga, etc, acid activation, ion exchange with transition metals and by metal oxide impregnation.

Alkylation of phenols is important in chemicals industries particularly in the agrochemical and pharmaceutical industries. (Fiege et al, in Gerhartz W., et al eds. 1987 – Valmann Encyclopedia of Industrial Chemistry, 5<sup>th</sup> edition, Wemheim, VCH Verlagsgesellschaft, Lowenheim F. A. et al, 1975, Industrial Chemicals, A. Wiley InterScience, New York, Kirk, J., et al, 1981, Encyclopedia of Chemical Technology, 3<sup>rd</sup> edition, Wiley, New York). Alkylation of phenol methanol over various catalysts has been studied (Nozaka et al, Bull. Chem. Soc. Japan, 50, 1997, 614; Narayanan et al, J. Mol. Catal., 52, 1987, 129; Velu et al, React. Kinetic Catal. Lett. 62(2), 1997, 339 and Appl. Catal. A. General, 119, 1994, 241). Karuppanasamy et al report the alkylation of phenol with alcohol over thoria (J. Catal. 63, 1980, 433). Klemm et al report the alkylation of phenol with 2-propanol (J. Org. Chem., 45, 1980, 4326). Alkylation of isopropanol over zeolite catalyst is reported in Guo Changwan et al (Beijing Huagong Yanjiuyuan, 27(3), 1998, 163). Tertiary butylation of phenol was carried out over acid catalyst (Corma et al, J. Catal. 134, 1992, 58 and Appl. Catal. 105, 1993, 271). Peimo et al report the tertiary butylation of phenol over zeolite solid acid catalyst in vapour phase (Huadong Huadong Xueyan Xuebao, 14(4), 1998, 476; See also Chang et al – US Patent 5288927 and Kuizhang et al., Appl. Catal. A. General, 166, 1998, 89).

Alkylation of dihydroxy benzene with tertiary butyl alcohol using mineral acids was investigated by Korneev et al (USSR Patent 1583407, 1990).

The prior art processes above suffer from the following disadvantages:

1. Catalyst cannot be reused
2. Disposal of the acids used is not environmentally safe and/or economical
3. The selectivity is frequently observed to be low
4. Corrosion of the reactors and the reaction vessel
5. The process and the reactants are not easily handled
6. Large amounts of catalyst are required

It is therefore necessary to develop a process that overcomes the drawbacks enumerated above.

### Objects of the invention

The main object of the invention is to develop a process for the preparation of dihydroxybenzene which overcomes the drawbacks of the prior art enumerated above.

Another object of the invention is to develop a process for the preparation of alkylated dihydroxybenzene which is safe and economical.

A further object of the invention is to develop a process for the preparation of alkylated dihydroxybenzene wherein the catalyst can be recycled.

- 5 Yet another object of the invention is to develop a process for the preparation of alkylated dihydroxybenzene wherein the amount of catalyst required is less leading to savings in costs.

These and other objects of the invention are achieved by the process of the invention detailed below.

## 10 Summary of the invention

- Accordingly the present invention provides a process for the preparation of alkylated dihydroxybenzene, said process comprising alkylating dihydroxy benzene with tertiary butyl alcohol in the presence of a catalyst at a temperature in the range of 40 to 90°C for a time period in the range of 2 to 8 hours, separating the alkylated
- 15 dihydroxybenzene.

In one embodiment of the invention the dihydroxybenzene is selected from the group consisting of resorcinol, hydroquinone and catechol.

- In another embodiment of the invention, the catalyst used is selected from zeolites of the types HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ ), HY ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$ ), H-Mordenite (HM) ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ ), MCM-41, Montmorillonite -K10 clay, alumina
- 20 and polyaniline sulfate.

In another embodiment of the invention, the reaction is carried out at a temperature in the range of 60 to 90°C.

- In a further embodiment of the invention, the reaction is carried out for a time
- 25 period in the range of 6 to 8 hours.

## Detailed description of the invention

- The process of the invention uses solid acid or polyaniline sulfate as the catalyst for the alkylation of dihydroxybenzene with tertiary butyl alcohol. The dihydroxybenzene is generally resorcinol, hydroquinone and catechol. Zeolites of the
- 30 types HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ ), HY ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$ ), H-Mordenite (HM) ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ ), MCM-41, Montmorillonite -K10 clay, alumina and polyaniline sulfate are used as the catalyst for the process of the invention.

The reaction is preferably carried out at a temperature in the range of 60 to 90°C and for a time period in the range of 6 to 8 hours.

The catalyst can be removed by any conventional method such as filtration followed by separation of the alkylated product by conventional column chromatography using adsorbents such as silica gel, alumina and a solvent such as chloroform, ethylacetate, hexane and any mixture thereof. The catalyst can be recycled to the reaction mixture.

The following examples are illustrative and should not be construed as limiting the scope of the invention in any manner.

#### 10 Example 1:

2.8 ml of tertiary butyl alcohol was taken in 50 ml round bottom flask and 1 g of resorcinol and 200 mg of catalyst was added. The reaction mixture was refluxed at 80°C for 8 hours. The reaction mixture was then filtered and the filtrate analysed using a CHEMITO 8510 Gas Chromatography using 20% SE-30 column coupled with flame ionisation detector for product distribution.

Gas Chromatography –Mass spectral fragmentation pattern and Proton Nuclear Magnetic Resonance spectra (<sup>1</sup>HNMR) of the products proves that the products obtained are a mixture of mono and dialkylated benzene.

The different catalysts used and the conversion and selectivities are given in Table 1 below:

**Table 1:** conversion and selectivities using different solid acid catalysts

Solid acid catalyst	Conversion of resorcinol (%)	Selectivity (%)	
		4- <i>t</i> -butyl resorcinol	4,6-di- <i>tert</i> -butyl resorcinol
HZSM-5	6	100	
HY	44	77	23
HM	18	84	16
MCM-41	15	96	4
Montmorillonite –K10	3	100	
Modified montmorillonite K-10	99	27	73

#### Example 2:

2.8 ml of tertiary butyl alcohol was taken in 50 ml round bottom flask and 1 g of resorcinol and 200 mg of catalyst was added. The reaction mixture was refluxed at 80°C for 2, 4, 6 and 8 hours, filtered and the product analysed. The reaction was

carried out using modified montmorillonite K10 solid acid catalyst and the conversion and selectivities are given in Table 2 below.

**Table 2:** conversion and selectivity with change in reaction time

Reaction time (hours)	Conversion of resorcinol (%)	Selectivity (%)	
		4-t-butyl resorcinol	4,6-ditertiary butyl resorcinol
2	28	86	12
4	2	46	54
6	81	58	42
8	99	27	73

**5 Example 3:**

2.8 ml of tertiary butyl alcohol was taken in 50 ml round bottom flask and 1 g of resorcinol and 200 mg of catalyst was added. The reaction mixture was refluxed at 80°C for 8 hours. The temperature of the reaction mixture was varied from 60 to 90°C in steps of 10°C. The reaction product was filtered and analysed. The reaction was

**10** carried out using modified montmorillonite K10 solid acid catalyst and the conversion and selectivities are given in Table 3 below.

**Table 3:** conversion and selectivity with change in reaction temperature

Temperature of the reaction (°C)	Conversion of resorcinol (%)	Selectivity (%)	
		4-t-butyl resorcinol	4,6-ditertiary butyl resorcinol
60	7	100	
70	33	84	16
80	42	79	21
90	99	27	73

**Example 4:**

**15** 2.8 ml of tertiary butyl alcohol was taken in 50 ml round bottom flask and 1 g of resorcinol and 200 mg of catalyst was added. The reaction mixture was refluxed at 80°C for 8 hours. The mole ratio of resorcinol to tertiary butyl alcohol was varied in the following: 1:3, 1:5, 1:7, and 1:9. The reaction product was filtered and analysed. The reaction was carried out using modified montmorillonite K10 solid acid catalyst

**20** and the conversion and selectivities are given in Table 4 below.

**Table 4:** conversion and selectivity with change in molar ratios of resorcinol and tertiary butyl alcohol

Molar ratio of resorcinol to tertiary butyl alcohol	Conversion of resorcinol (%)	Selectivity (%)	
		4-t-butyl resorcinol	4,6-ditertiary butyl resorcinol
1:3	99	27	73
1:5	33	79	21
1:7	30	80	20
1:9	10	91	9

**Example 5**

- 5        2.8 ml of tertiary butyl alcohol was taken in 50 ml round bottom flask and 1 g of hydroquinone and 200 mg of modified montmorillonite – K10 catalyst powder was added. The reaction mixture was refluxed at 80°C for 8 hours. The conversion of hydroquinone was found to be around 57%.

**Example 6:**

- 10       2.8 ml of tertiary butyl alcohol was taken in 50 ml round bottom flask and 1 g of catechol and 200 mg of modified montmorillonite solid acid catalyst powder was added. The reaction mixture was refluxed at 80°C for 8 hours. The conversion of catechol was found to be around 45 %.

**Example 7:**

- 15       2.8 ml of tertiary butyl alcohol was taken in 50 ml round bottom flask and 1 g of resorcinol and 200 mg of polyaniline sulfate catalyst was added (for preparation of catalyst see *Composition and spectral studies of polyaniline salts*, S. Palaniappan, *Polymers for Advanced Technology*, 5, 1994, 225). The reaction mixture was refluxed at 80°C for 8 hours. The reaction mixture was then filtered and the product
- 20       analysed. The conversion and selectivities are given in Table 5 below.

**Table 5:** conversion and selectivity with change in molar ratios of resorcinol and tertiary butyl alcohol and using polyaniline sulfate catalyst

Molar ratio of resorcinol to tertiary butyl alcohol	Conversion of resorcinol (%)	Selectivity (%)	
		4-t-butyl resorcinol	4,6-ditertiary butyl resorcinol
1:3	51	73	27
1:5	41	34	66

**Advantages of the invention**

1. The use of solid acid catalysts or solid polymer catalysts in the liquid phase alkylation of dihydroxy benzene with tertiary butyl alcohol is done for the first time.
- 5 2. High catalytic activity and selectivity are observed.
3. The solid acid catalyst does not corrode the reaction vessel.
4. Repeated use of the catalyst is possible allowing recycling of the catalyst to the reaction vessel.
5. The turn over frequency is improved.
- 10 6. Separation of the catalyst from the reaction mixture is easy
7. Disposal of the solid acid catalysts is not a problem since they are environmentally safe.

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**We claim:**

1. A process for the preparation of alkylated dihydroxybenzene, said process comprising alkylating dihydroxy benzene with tertiary butyl alcohol in the presence of a solid acid/solid polymer catalyst at a temperature in the range of 40  
5 to 90°C for a time period in the range of 2 to 8 hours, separating the alkylated dihydroxybenzene.
2. A process as claimed in claim 1 wherein the dihydroxybenzene to be alkylated is selected from the group consisting of resorcinol, hydroquinone and catechol.
3. A process as claimed in claim 1 wherein the catalyst used is selected from zeolites  
10 of the types HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ ), HY ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$ ), H-Mordenite (HM) ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ ), MCM-41, Montmorillonite -K10 clay, alumina and polyaniline sulfate.
4. A process as claimed in claim 1 wherein the reaction is carried out at a temperature in the range of 60 to 90°C.
- 15 5. A process as claimed in claim 1 wherein the reaction is carried out for a time period in the range of 6 to 8 hours.

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## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/IN 01/00068A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07C39/08 C07C37/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 965 039 A (CHAPLITS DONAT NIKOLAEVICH ET AL) 22 June 1976 (1976-06-22) example 8	1,2
A	FR 2 104 085 A (UNION RHEINISCHE BRAUNKOHLN KRAFTSTOFF AKTIENGESSELLSCHAFT) 14 April 1972 (1972-04-14) page 1	1
A	GB 761 613 A (EASTMAN KODAK CO) 14 November 1956 (1956-11-14) claims	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3965039	A	22-06-1976	NONE	
FR 2104085	A	14-04-1972	DE 2039123 A1 BE 770830 A1 CH 547245 A FR 2104085 A5 GB 1315905 A NL 7110417 A	10-02-1972 16-12-1971 29-03-1974 14-04-1972 09-05-1973 08-02-1972
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